Chemical Equilibrium and Le Chatelier's Principle

PRELIMINARY READING: Chang, section 14.5

INTRODUCTION

Although for practical purposes many chemical reactions are considered to proceed to completion, on the molecular level nearly every chemical reaction may in principle be considered to be reversible. Consider the following hypothetical reaction:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D \qquad (1)$$

where A, B, C, and D represent chemical species and a, b, c, and d represent the coefficients of each species in the balanced equation. The double arrow between the reactants and products signifies that this is a reversible reaction. The condition of **chemical equilibrium** is attained when the concentrations of the reactants and products are no longer changing. The **equilibrium constant K_c** is defined by the following expression:

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad (2)$$

in which the square brackets signify molar concentrations of each species. The expression on the right-hand side of equation (2) is sometimes called the mass-action expression for the reaction. Once a reaction has reached equilibrium, the numerical value of the mass-action expression will always equal the constant value K_c as long as the temperature remains constant. If any one of the concentrations should change, the concentrations of all other species must change in order to maintain the same value of the equilibrium constant. This idea is stated in the following form as **Le Chatelier's Principle**:

If a stress is applied to a system at chemical equilibrium, the equilibrium will shift in such a manner as to counteract the effects of that stress.

The stress may be a change in the concentration of a species, a change in temperature, or a change in pressure. In this experiment we will observe and interpret the effects of changes in concentration (addition or subtraction of reagents) and temperature upon systems at equilibrium.

PRE-LAB EXERCISES

Assume that the following reaction is in chemical equilibrium:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) + \text{heat} \qquad (3)$$

Explain the effect of each of the following changes upon the system in terms of Le Chatelier's Principle and a shift toward either the product or reactant side.

1. More hydrogen is added to the system.
2. Ammonia is removed from the system.
3. Nitrogen is removed from the system.
4. The temperature is raised.
5. The pressure of the system is decreased by doubling the total volume.

EQUIPMENT: 24-well culture plate, wash bottle, Pasteur pipet and bulb, one large test tube, three small test tubes, 50-mL Erlenmeyer flask, test tube rack, test tube clamp, two 250-mL beakers, ring stand, iron ring, wire gauze, burner, flint striker

EXPERIMENTAL

<u>**Note**</u>: A number of extremely hazardous corrosive chemicals, e.g., concentrated HCl, is used in this experiment. Use all appropriate safety precautions. Concentrated HCl must be used in the hood. If you spill any of this reagent on yourself, immediately rinse it off with large amounts of running water and inform the instructor. **The laboratory dress**

code will be strictly enforced!

As you carry out each procedure, carefully record your observations in your laboratory notebook. Do not answer the questions in the laboratory manual at this time (do this in the report). The different parts of the experiment may be carried out in any order. All solutions may be rinsed down the drain with plenty of water when you are finished.

1. Iron(III) Ion with Thiocyanate Ion

The reagents are preloaded in Beral pipets (plastic droppers). Combine 2 drops of 0.2 *M* $Fe(NO_3)_3$ and 4 drops of 0.1*M* KSCN in one well of the culture plate. Add 40 drops of deionized water and mix thoroughly. Note the colors of each reagent and of the product. The two reagents combine to form a complex ion according to

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq) \qquad (4)$$

Note: potassium ion and nitrate ion are both colorless spectator ions. Divide the solution among three wells of the plate. Note the color; this will be used as your reference point for the original system, which contains all three species (it will be helpful to place a piece of white paper underneath the culture plate). To the first portion, add 5-8 drops of $Fe(NO_3)_3$, mixing after each drop, and observe all changes carefully (you may add more than 8 drops if necessary to observe a change). To the second, add 5-8 drops of KSCN, mix, and observe. To the third well, add 5-8 drops of 6 *M* NaOH, mix, and observe (mixture may need to stand for several minutes). **Note:** the compound iron(III) hydroxide, $Fe(OH)_3$, is quite insoluble in water. Clearly explain all of your observations in terms of Le Chatelier's Principle. **Question:** If you are told that the mercury(II) ion combines with thiocyanate to form the compound $Hg(SCN)_2$, which is soluble but <u>undissociated</u> in water, predict the effect upon the equilibrium of equation (4) if mercury(II) ion were added to the system.

2. Ammonium Nitrate with Water

Fill a large, dry test tube to a depth of about 2-3 cm with solid ammonium nitrate. Add a volume of water equal to about one-half of the volume of the solid and shake to mix; do not dissolve all of the solid. Observe any temperature change (qualitatively). The system may be described by the following equation:

$$NH_4NO_3(s) + H_2O(l) \rightleftharpoons NH_4NO_3(aq) \qquad (5)$$

Heat may be regarded as a reactant or product in chemical reactions. Heat is absorbed (reactant) in endothermic reactions; heat is evolved (product) in exothermic reactions. Determine whether this reaction is endothermic or exothermic and rewrite the equation explicitly including heat as a reactant or product to show this. **Predict** the effect upon the system of raising the temperature and **test** your prediction experimentally.

3. Cobalt(II) Ion, Water, and Chloride Ion

Solid salts of cobalt(II) typically are found as hexahydrates of formula $CoX_2 \cdot 6H_2O$, in which X may be any of several mononegative anions such as nitrate or chloride. Notice that such a compound must be electrically neutral overall. The six water molecules are actually bound to the metal, and must be taken into account in calculating the formula weight. In aqueous solution, the pink octahedral complex ion $[Co(H_2O)_6]^{2+}$ (hexaaquacobalt(II) ion) maintains its identity. However, in the presence of excess chloride ion it is possible to form the blue tetrahedral complex ion $[CoCl_4]^{2-}$ (tetrachlorocobaltate(II) ion). Part 3 of this experiment will examine the equilibrium between these two complex ions:

$$[Co(H_2O)_6]^{2+} + 4\ Cl^{-} \rightleftharpoons [CoCl_4]^{2-} + 6\ H_2O \qquad (6)$$

Note that in dilute aqueous solutions the concentration of water is very high (about 55 M); thus, the octahedral complex normally predominates.

A. Concentration Effects

Place 5 drops of 0.4 *M* $Co(NO_3)_2$ (Beral pipet) in an empty well of the culture plate. This solution exhibits the color of the hexaaquacobalt(II) ion (remember that nitrate is colorless). Half-fill another well with 12 *M* HCl **(CAUTION!)**. Use a Pasteur pipet to add 12 drops of this HCl to the $Co(NO_3)_2$ solution, mixing thoroughly and observing **after each drop**. Now add 20 drops of water to the same well in small increments, mixing and observing as before. Explain all observations.

Now add enough anhydrous calcium chloride to the same well to form a layer covering the bottom of the well. **<u>Do</u> <u>not</u>**

mix. The calcium chloride is a **desiccant** (look the word up), and should not completely dissolve. Let the mixture stand for several minutes before recording your observations. Explain what has happened (the chloride ion in the calcium chloride is not of significance).

B. Temperature Effects

Place 5 mL of 0.4 *M* $CoCl_2$ into a small flask and add 3 mL of concentrated hydrochloric acid, mixing thoroughly. The solution should be a magenta (red-violet) color; if it is not, add a few drops of water or HCl until a red-violet color is attained. Note that hydrogen ion and chloride ion are colorless. The solution now contains appreciable amounts of both major cobalt species in equation (6). Divide the solution equally among three test tubes. Maintain one test tube at room temperature, place the second in a boiling-water bath, and place the third in an ice bath. Observe. Switch the hot and cold test tubes (after allowing them to return to room temperature) in order to determine whether the changes are reversible. Explain all observations. Write out equation (6) including heat as a reactant or product and classify the reaction as either endothermic or exothermic.

4. Copper(II) Ion and Ammonia (Optional)

Place about 2 mL of copper(II) sulfate solution in a test tube. Note the color of the solution, which is due to the complex ion $[Cu(H_2O)_4]^{2+}$. Add dropwise 1 mL of ammonia solution, mixing and observing after each drop. The ammonia displaces water to form the complex ion $[Cu(NH_3)_4]^{2+}$, whose color is responsible for the final color of the solution. Write an equation for the reaction and interpret the changes in terms of Le Chatelier's Principle. Now add sulfuric acid dropwise to the previous solution, mixing and observing as before. Explain your results. Note that ammonia is a base which reacts with sulfuric acid as follows:

$$H_2SO_4(aq) + 2\ NH_3(aq) \rightleftharpoons 2\ NH_4^+(aq) + SO_4^{2-}(aq) \qquad (7)$$

THE LAB REPORT

For each part, first write the chemical equation for the equilibrium. Explain all observed changes in terms of Le Chatelier's Principle (what was the stress induced upon the equilibrium?) and a shift to one side or the other. Answer any questions from the lab manual in each part.

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